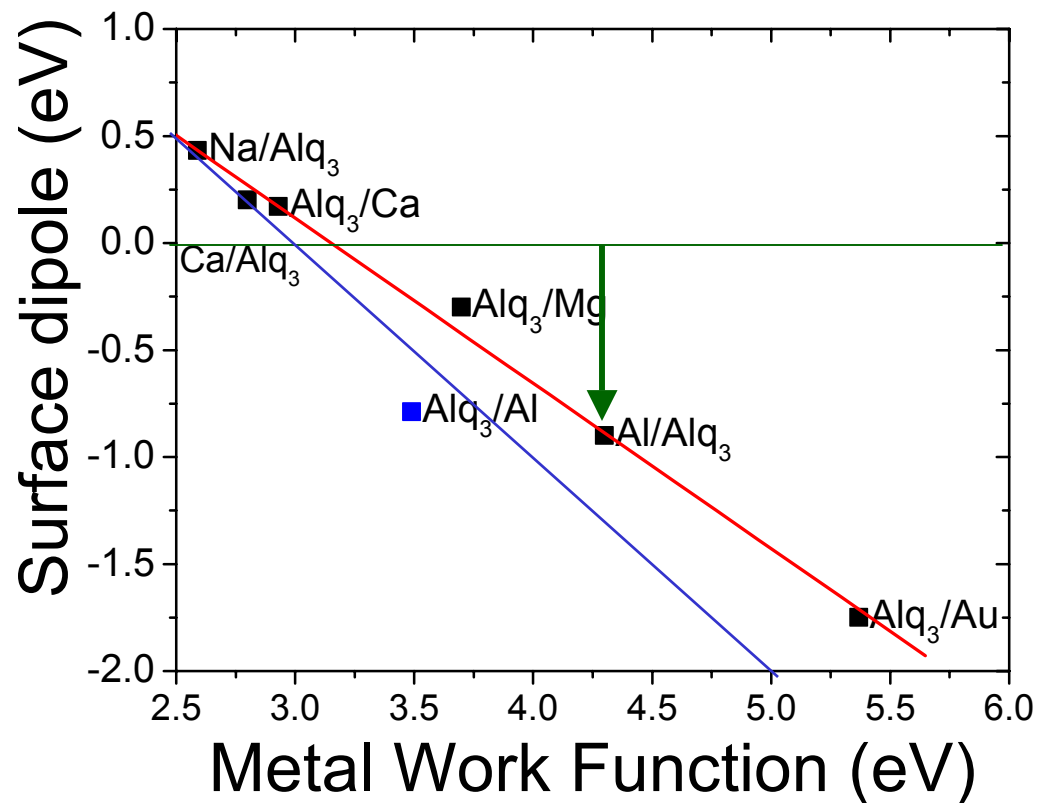


Interface Dipole vs. Workfunction

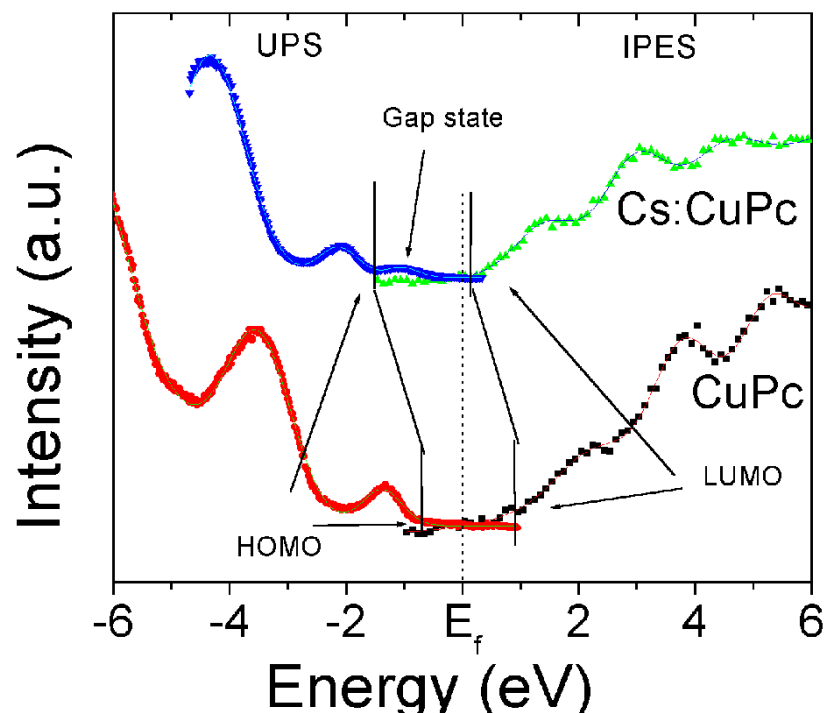


- V_{dipole} proportional to metal workfunction ϕ_M except Alq₃/Al
- The crossover not at midgap <- metal electron dipole?
- Change of slope for Na/Alq₃, Ca/Alq₃, and Alq₃/Al <- pinning at LUMO

Fig. 1. The interface dipole of metal and Alq₃ as a function of the metal workfunction, obtained from x-ray photoemission (XPS) and ultraviolet photoemission spectroscopy (UPS). The data fall closely to a straight red line, with a slope of -0.8. The linear dependence is an indication that the charge transfer and chemical bonding model (Tung, PRL **84**, 6078(2000)) is applicable to the interface systems. For low workfunction metals Ca and Na, the XPS and UPS energy level analysis actually indicates that the Fermi level is pinned at the Alq₃ LUMO. Once such pinning takes place, there'll be no further change of the organic energy level with respect to the Fermi level, and any change of the metal work function will be fully compensated by the interface dipole. This full compensation will result in a slope of -1 in the interface dipole vs. metal work function plot. The change of slope to -1 is indeed observed for Na/Alq₃, Ca/Alq₃ and Alq₃/Al as illustrated by the blue line in the figure. The result indicates that it is possible to predict the interface dipole and subsequent energy level alignment between organics and metals.

The thermodynamic equilibrium model by Tung intends to move the Fermi level toward the mid-gap of the semiconductor at $\chi_s + E_g/2$, and the interface dipole changes sign as the metal work function goes across the mid-gap energy. Our data, however, show an interface dipole potential of -0.9 eV from the mid-gap energy at 4.3 eV to the straight line derived from the interface dipole dependence on the metal work function. We attribute this apparent discrepancy from the thermodynamic equilibrium model to the pushing back of the electron cloud by the organic material. As the electron cloud tails out of the metal surface defined by the positive ion cores of the metal, the relative displacement of the charge density results in a dipole layer pointing away from the metal surface, and a negative dipole potential V_{dipole} seen by the electrons. When the electron cloud tail is pushed back by the organic material, its contribution to the metal work function is eliminated. The deviation of the dipole potential from the thermodynamic model by -0.9 eV is therefore the contribution of the electron tailing to the metal work function. The same contribution is expected to be in all the metal/organic systems since electron tailing is universal to all the metal surfaces.

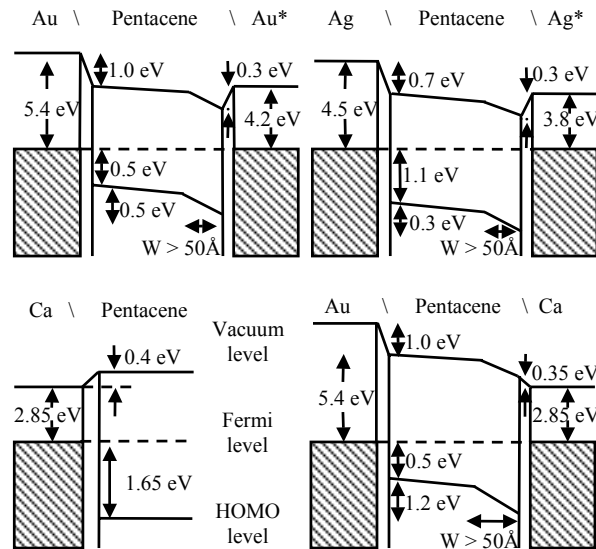
Pinning of Fermi Level at LUMO of CuPc



- PES and IPES data show a rigid shift of both the HOMO and LUMO
- The pinning of the Fermi level at the LUMO in Cs:CuPc clearly seen in the IPES spectrum

Fig. 2. Copper phthalocyanine has become an important ingredient in OLED for modifying the interface properties. Commonly considered as a p-type organic semiconductor, CuPc is traditionally used as a hole injecting material in OLED. Thus the use of alkali metal doped CuPc for electron injection is a totally new and unconventional approach. In Figure 2, the comparison of the electronic structure and energy level alignment of pristine and Cs doped CuPc is shown. The bottom part is from pristine CuPc . The upper part is of CuPc doped with Cs. The Cs doping concentration is determined to be about 0.85 by the XPS measurements. The onset of the LUMO position, obtained by the conventional method of extrapolating the leading edge of the spectrum, is less than 0.2 eV from the Fermi level. Given the instrument resolution of IPES (~ 0.6 eV), the Fermi level is virtually aligned with the LUMO of CuPc. We can similarly determine the onset of the HOMO position is about 1.5 eV below the Fermi level. This is the first direct observation of the Fermi level pinning at the LUMO.

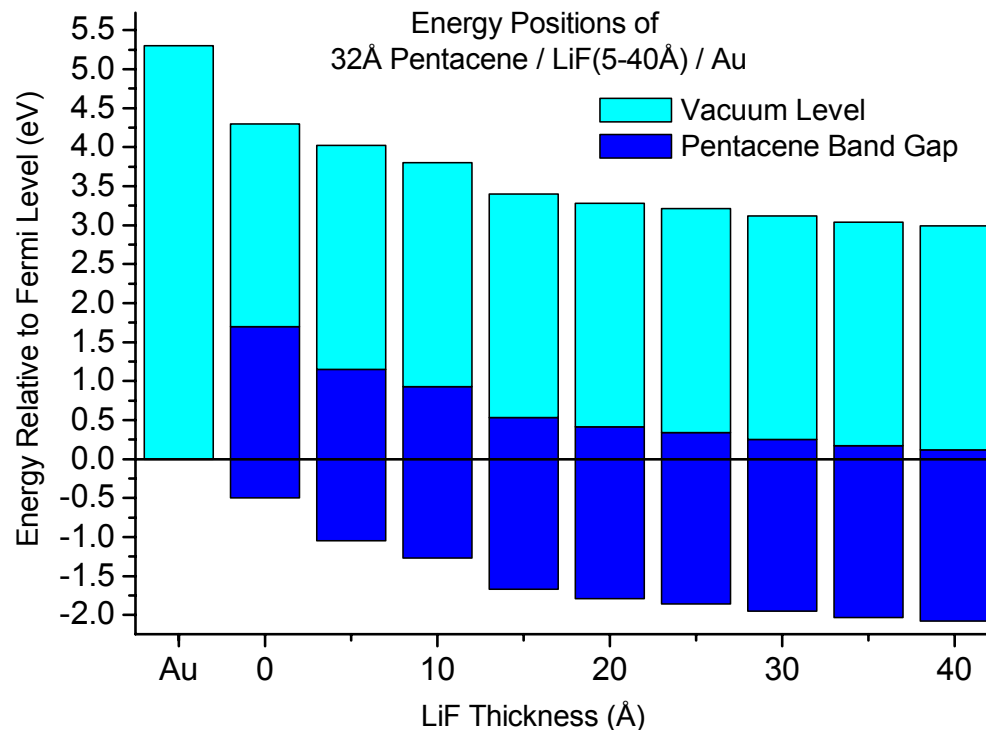
Symmetry of Pentacene Metal Interfaces



- Pc/Au (Pc/Ag) is different from Au/Pc (Ag/Pc)
- Pc/Ca is the same as Ca/Pc in terms of interface energy level alignment

Fig. 3 presents a summary of the results for the interfaces between pentacene and metals Au, Ag, and Ca. In the figure, the sequence of deposition is from the left to right. Both the Ag and the Au interface exhibit a measurable Fermi level after ~ 8 Å of metal deposition, indicating a metallic surface. Yet it can be clearly seen that neither metallic surface gives the work function of the pure metal, even after 30+ Å of metal deposition, nor the valence features of the clean metal surface. The Au on pentacene results in a work function of 4.3 eV, more than 1 eV lower than that of pure Au while Ag on pentacene gives a work function of 3.8 eV, 0.7 eV lower than that of pure Ag. We interpret this as indication that as these metals are deposited onto the pentacene surface the metal either first penetrates the surface, thereby doping the upper layers of the pentacene or diffuses into the pentacene. The attenuation of the C 1s XPS peak supports metal diffusion or clustering of Au and Ag. For the deposition rates used in these experiments, < 0.1 Å per second, it is more likely that the metal diffused into the pentacene. The subsequent doping region width, $w > 50$ Å, is estimated from XPS core level analysis. We have used Au* and Ag* in Figs. 3 and 4 to represent the metallic mixtures at these interfaces. The difference between metal on organic and organic on metal results in asymmetric electronic properties, for example the hole injection barrier is 0.5 eV for pentacene on Au but 1 eV for Au on pentacene.

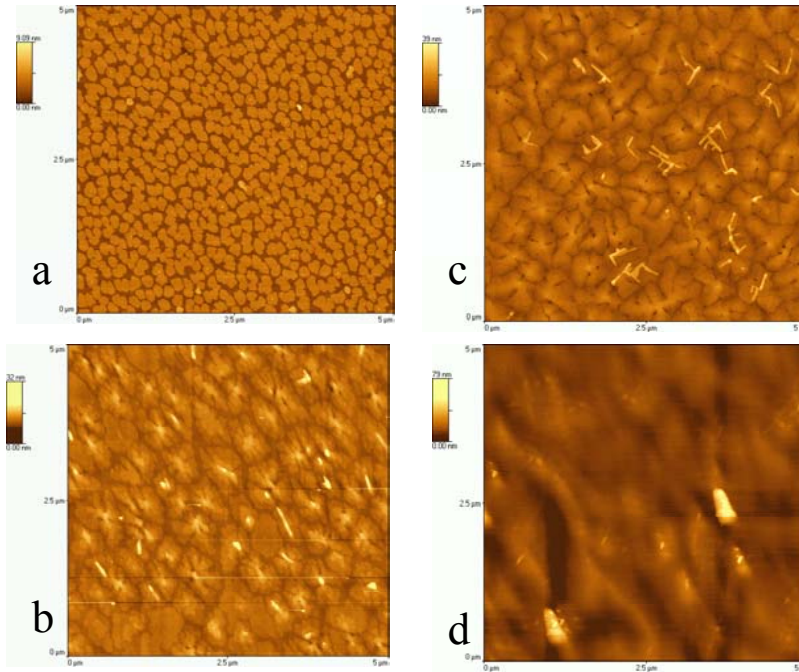
Organic/Insulator Interface: Pc/LiF



- The Pc vacuum level is aligned to that of LiF, and follows as it is lowered by increasing LiF thickness
- Insulator/organic interface is characterized by vacuum level alignment

Fig. 4. Shown in the figure is the pentacene energy positions as a function of LiF film thickness. In this experiment, a wedged LiF film with thicknesses ranging from 5-40 Å is deposited onto a Au surface, and then pentacene is deposited onto the LiF film. The vacuum level of the LiF decreases from 4.3 to 3.5 eV above the Fermi level as the film thickness increases. The energy position of the subsequently deposited pentacene film follows precisely this decrease, and the vacuum level of the pentacene film is in alignment with the LiF. This is in sharp contrast to the interface dipole formation between metal and organic materials presented in Figs. 1-3. We've also studied other insulator/organic interfaces, including pentacene on SiO₂ and Al₂O₃. All the cases demonstrate that insulator/organic interface is characterized by alignment at the vacuum level.

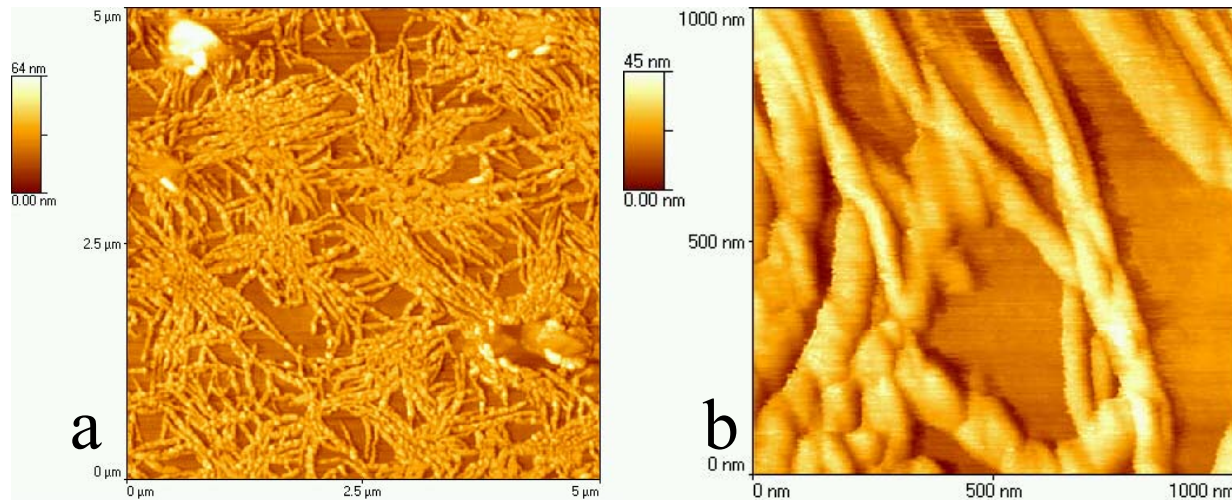
AFM Images of Pentacene on SiO₂



- Monolayer step size seen for the first layer.
- Later growth dendritic grains about 1 μm.

Fig. 5 shows the tapping mode images of pentacene films on SiO_2 substrate. All images are $10 \times 10 \mu\text{m}$. We observe a layer by layer growth of pentacene on SiO_2 substrate with full coverage at an average thickness of 20 \AA . In Fig. 4 a we can see first monolayer steps of pentacene developing, and forming the dendritic grains of about $1 \mu\text{m}$ in size (Fig. 4 b-d). From the line analysis, we obtained the step size of the monolayer steps to be about 15 \AA , which is the length of one pentacene molecule. The mobility measurements have shown that pentacene films on SiO_2 with such dendritic grains have higher mobility than the ones with granular structure obtained by flash evaporation on the same kind of substrate. So in fact, high mobility can only be obtained if the pentacene film is highly ordered.

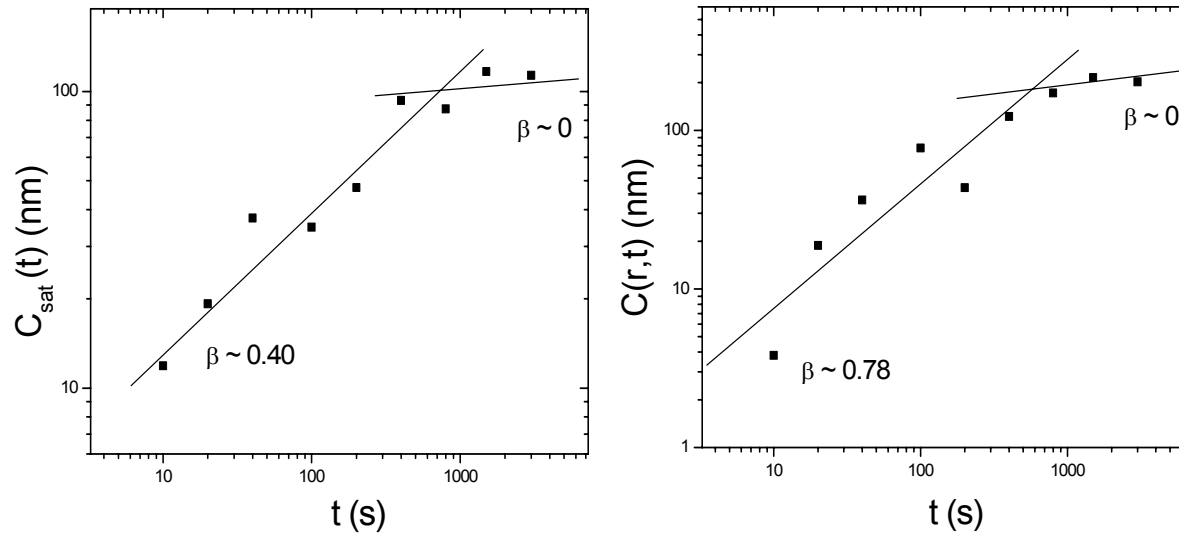
AFM Images of Pentacene on MoS₂



- Pentacene on MoS₂ grows in granular or snowflake mode.
- In the granular mode, pentacene forms wire like structure with diameter ~ 100 nm.

Fig. 6 shows the tapping mode images of pentacene films on MoS₂ substrate. We have observed two different growth modes for pentacene on MoS₂ substrate: snowflake like growth and granular growth. For the granular growth, the molecules are highly mobile and they form their own groups. Fig. 4a is 5x5 micron and Fig. 4b 1x1 micron. It shows that in the granular mode pentacene forms long wire-like structure on MoS₂. The diameter of those structures is about 100 nm and their length is about 1 μm. With better evaporation conditions these properties might be improved. It is very interesting to see these long nano-wires self organized on MoS₂ surface. Such wire like structure has never been observed for more interactive substrates like SiO₂ and Au. The interaction between pentacene and MoS₂ indicate that the nano-wire formation is an intrinsic property of pentacene, which may be useful for device applications.

Growth Mode of Perylene on Glass and on Au



- Height-height correlation shows non-stationary growth

Fig. 7. The equal-time height-height correlation function $C(r,t)$ of (a) perylene/glass and, (b) perylene/Au as a function of distance r plotted in a log-log scale for $R = 0.15$ and 10.00 \AA/s from top to bottom respectively. With increasing deposition rate, time dependence of the growth gets less dominant but does not disappear. The perylene growth type in this experiment is a non-stationary growth as the plots in the figure show clearly that $C(r)$ has a time dependence in the short-range. This indicates that normal dynamic scaling breaks down for perylene on these two substrates and that the local structure in these films changes a lot during film growth. However, increasing the deposition rate detracts from domination of local effects and makes the local structure stabilized. The perylene film growth was non-stationary within about two orders of magnitude of the deposition rate. Obviously perylene crystallization does not scale in a normal way. However, these findings offer a clue into the workings of the organic growth.

Education and Human Resource

- Graduate Students
 - Neil Watikns
 - Serkan Zorba
 - Li Yan (partially)
- Visiting Scientist
 - Akinori Tanaka (Tohaku University, Japan)
- Equal-time height-height correlation function $C(r,t)$ of perylene/glass and perylene/Au as a function of distance r

Prof. Yongli Gao's research group at the University of Rochester (DMR-9982988) focuses on the interfaces in organic semiconductors. In addition to the research achievements, it also presents strong commitment and contribution to education and development of human resources. Supported by NSF Grant are two graduate students, Neil Watkins and Serkan Zorba. Another graduate student, Li Yan (PhD., March 2002), is partially supplemented by the Grant.

All are in the Department of Physics and Astronomy. Serkan Zorba is from Turkey and Li Yan from China. Dr. Akinori Tanaka, a visiting scientist from Tohoku University, joined us and participated in the research for 6 months in 2001.